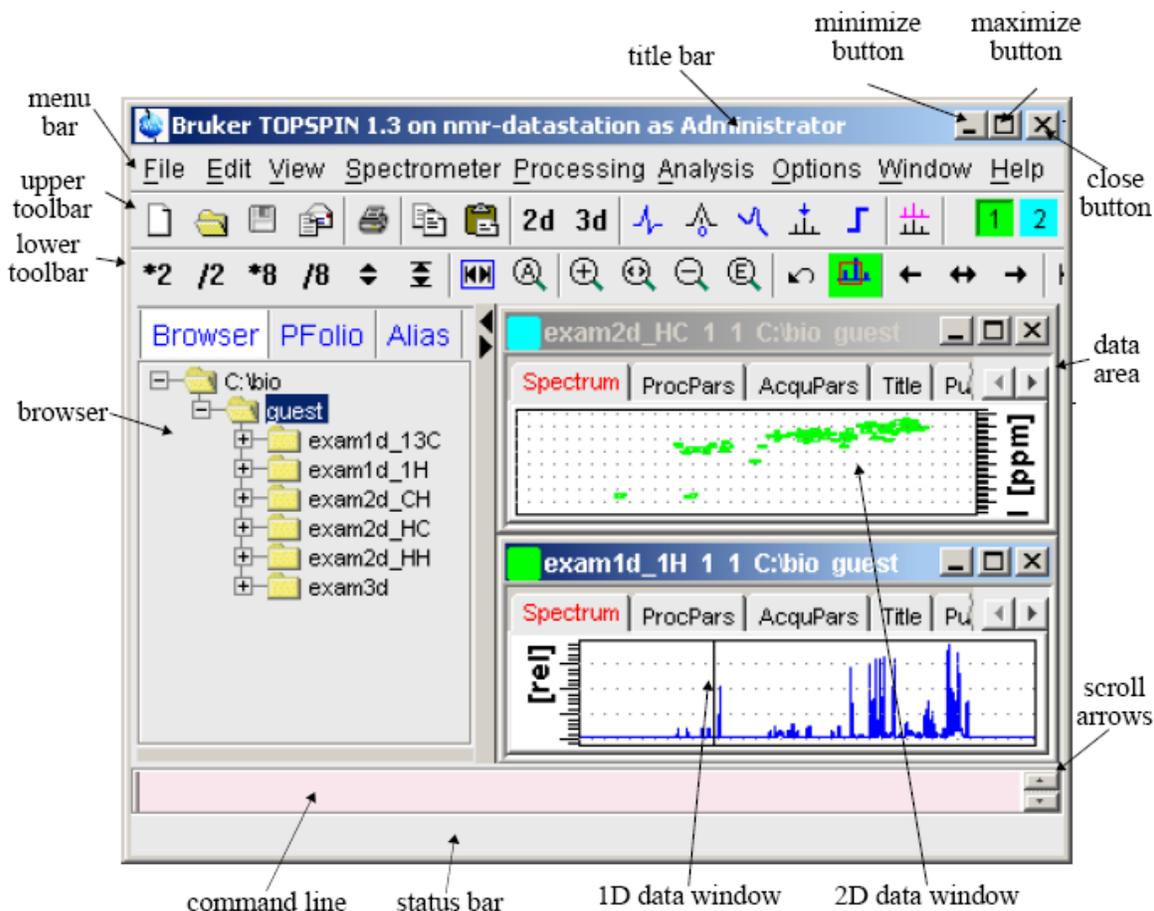


1D Solid-state NMR Procedure

(Bruker AVANCE Machines running TopSpin under WINDOWS XP)

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Safety Issues



If you have metal implants, DO NOT do NMR yourself.



Be aware of High Radio-Frequency Power in Solid-state NMR.



Take everything ferromagnetic or vulnerable to magnetic field, such as mechanic watches, cellular phones, keys, credit cards, bank cards, tapes, computer disks, etc., out of your pockets and put them somewhere away from magnets.

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I. Sample preparation

- Sample volume: about 100mg and 200mg for organic and inorganic samples, respectively.
- Make sample dry and as pure as possible.
- Ground sample to powder without chunky pieces.
- Using packing tools to pack sample into a rotor as uniform as possible, press sample with presser for more sample (But DON'T break the presser !!!). Leave ~2mm space at the top for cap.
- Cap the rotor with bare hands only and clean the outside of the rotor with ethanol-rinsed napkin.
- Paint half of the bottom edge of the rotor to black using a Permanent Marker for spinning speed detection.

II. Sign onto Logsheet

Enter

1. your name
2. your advisor's name and department
3. your recharge account number (in the format: 8-4XXXXX-XXXXX-3)
4. your start time
5. **(Do this at the end of experiment:** your stop time and duration of experiment)
6. **(Do this at the end of experiment:** Status of instrument and report problems if any)

III. Start TopSpin Software

1. Make sure that the spectrometer is idle by looking at the computer. If so, proceed to Step 2 below (if not, either wait, talk to the user, or do something else)
2. Login into the WINDOWS computer
Type your username, hit the Tab key
Type your password, hit return
3. Double click the TopSpin icon  on the desktop, the last dataset from your previous login session will appear. (The first time you login, you may see a license agreement window. Choose *Accept* and then *OK*).



Power of right-click provides more functions and options. If you cannot find something you want, try the right mouse button.

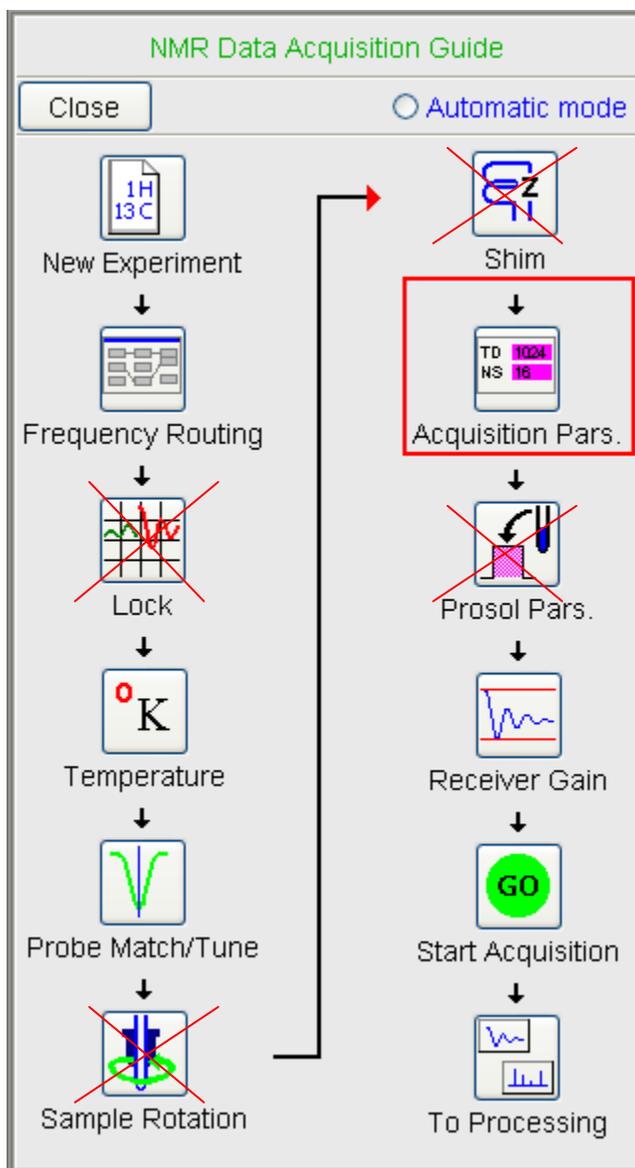
V. Setup and Data Acquisition

 Please ask for help the first time you start a new experiment or observe a new nucleus. Talk to Jerry in advance (x7940 or jghu@mrl.ucsb.edu).

Important:

- Make sure that the parameters set you are going to load is for solids (ask Jerry if not sure).
- Don't play with power parameters "p11", "p12", "p111", "p112", etc. if you don't know how, or probe and/or your sample may be burnt.

Click *Spectrometer* → *Data Acquisition Guide*, the flow chart below appears at the right side of the data area:

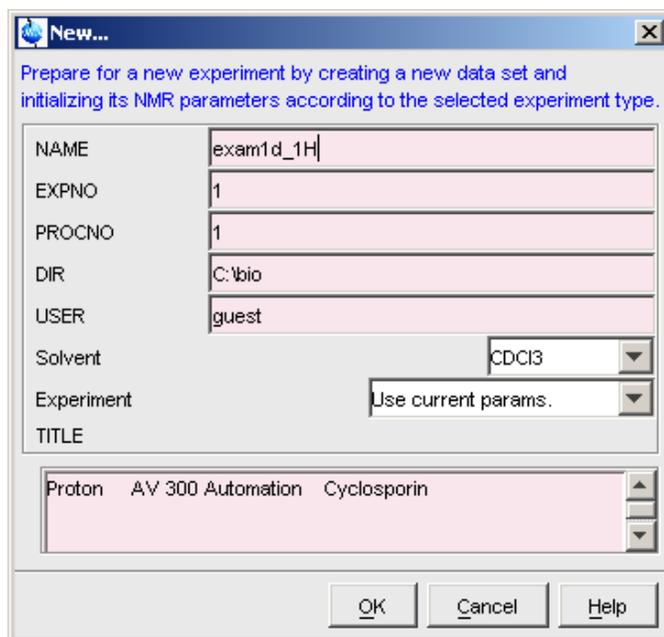


By sequential clicks on all the buttons except **Lock, Sample Rotation, Shim and Prosol Pars***, the Acquisition guide will walk you through the data acquisition process interactively. At each step, a dialog window will open to offer you the available choices and required parameters.

*  For solid-state-NMR experiments, those four steps are not required and therefore will be skipped.

1. Pull out and display the experiment in the data area of TopSpin:
 - i. Go to the Browser on the left of TopSpin window;
 - ii. Go down the directory tree to the experiment;
 - iii. Right-click and hold on the corresponding EXPNO and choose “DISPLAY”.

2. Click on **New Experiment**  (or *File* → *New*) [*New*] (Words in brackets are the corresponding commands): a window pops up where you can set the following parameters:



Name*:	e.g. $^{13}\text{C_CPMAS_Gly}$	(meaningful or descriptive)
EXPNO*:	1	(start with 1)
PROCNO:	1	(start with 1)
DU:	C:\Bruker\TOPSPIN	(don't change)
USER:	(your loginname)	(e.g. smith)
TYPE:	nmr	(don't change)
Solvent:	(meaningless for solids NMR)	
Experiment:	choose “Use Current Params” if you want to run the same experiment as the current data in display.	

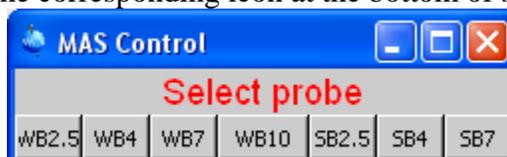
Title: (any information useful for current sample, project, and/or experiment)

Click **OK** to save changes and close the **New ...** window.

* : IF YOU DO NOT CHANGE EITHER THE NAME OR THE EXPNO OF YOUR DATASET, YOU MAY OVERWRITE YOUR OLD DATA AND LOSE IT FOREVER.

3. Insert Sample and Start MAS:

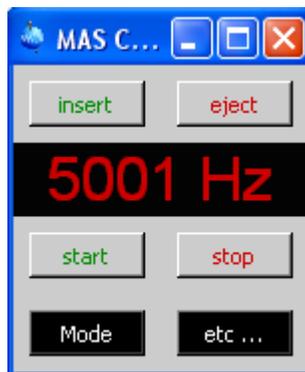
- Click on the  button in the upper toolbar. If the window below is not seen, click on the corresponding icon at the bottom of screen.



→ Click **WB4** (for 4mm rotors)



→ Click **Mode**

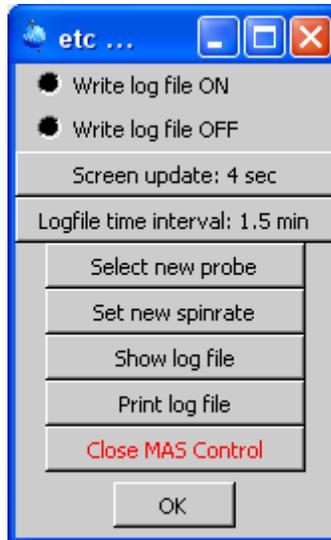


- (**Important:** It is important to make sure there is no sample already inside the magnet.) In the pop up window, see if the reading is zero first. Click **Eject** if it is, otherwise **Stop** and wait for spinning to go down to zero, and then click **Eject**.

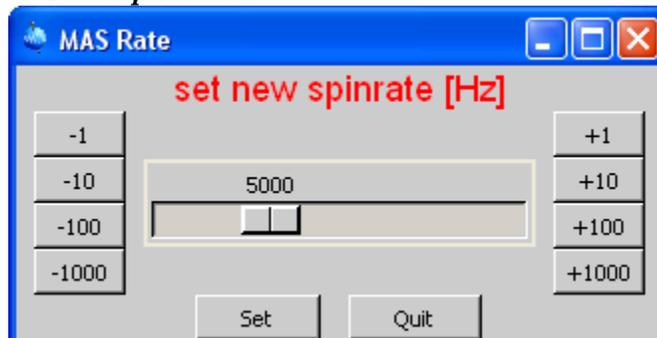


Insert pushes the sample to the correct location;
Eject blows the sample out to the top of magnet;
Start initiates spinning;
Stop stops spinning.

- Load the sample from the top of the magnet by removing the sample catcher (if there is one) and dropping the sample in the hole of the transfer line with the painted end down;
- Click **Insert** in the **MAS Control** window.
- To change the target spinning rate, click on **Etc ...**



→ Click *Set New Spinrate*



→ Click the desired buttons for the desired rate. For example, click **+1000** five times for 5kHz. For a newly packed sample, start with a low spinning, e.g. 3kHz.



You may test spinning on the MAS test station in the lab for a new sample.

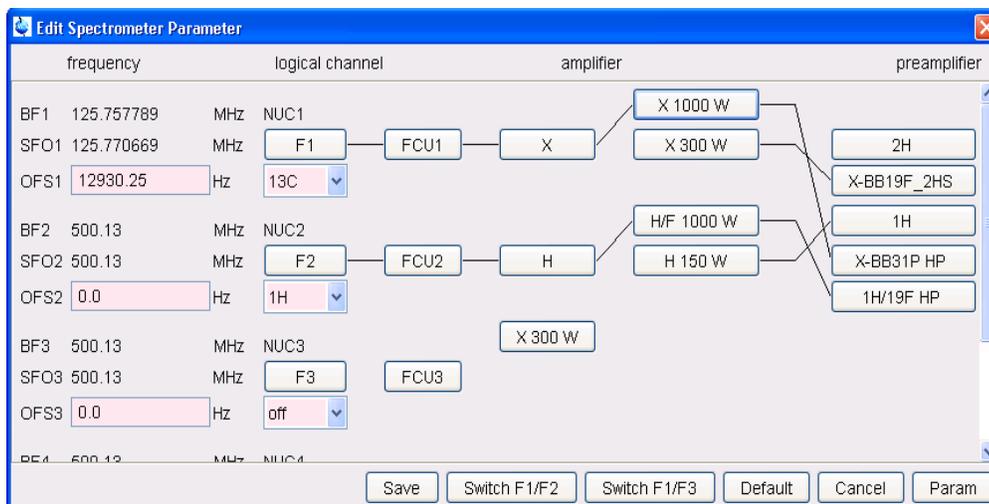
→ Click *Set*



To change spinning reading update rate, in the **Etc ...** window click ***Screen Update 12.0s*** → Double click the desired rate.

- In the **MAS Control** window, click ***Start*** button to start spinning and wait for the spinning to stabilize (which normally takes half a minute).
- If spinning is stable at a low rate, go back to **MAS Rate** window, increase the target rate, and click ***Set***. Repeat the process until the desired rate is set.

4. Click on the Frequency Routing icon  to check or change routings according to the experiment to be run. Except the connections between amplifiers and preamplifiers, all other connections can be modified (restrictions apply) by clicking on the corresponding button pair.



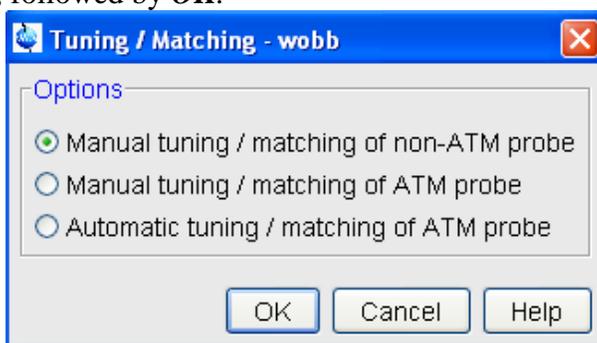
Click **Save** to validate changes and close the window.

5. (Optional)

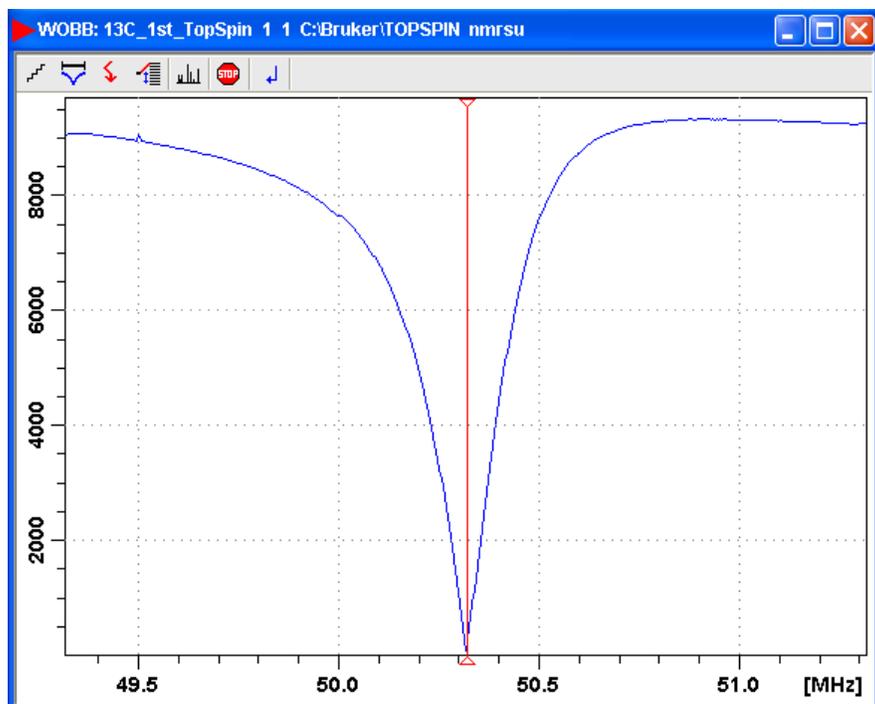
If you do VT experiments, click on **Temperature**  and set the desired temperature in the popping up window.



6. Click on **Probe Tune/Match**  and select “Manual tuning / matching of non-ATM probe”, followed by **OK**.



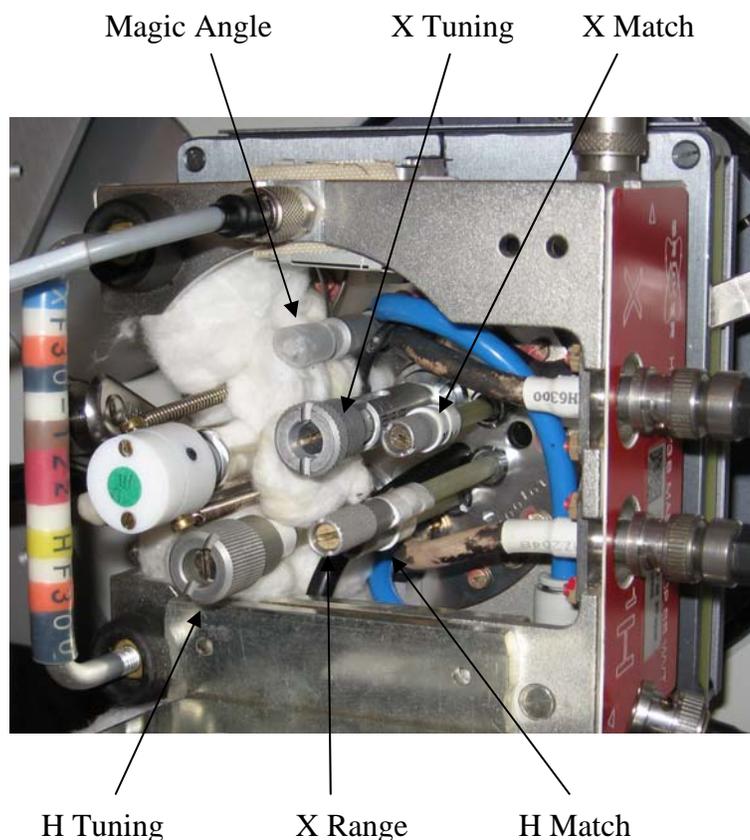
After ~20s, you will see a WOBB window showing the tuning/matching curve, the horizontal position of which corresponds to tuning and the depth to matching.



 The tuning curve should be aligned on the screen with the central redline and should reach all the way to the zero line of Y axis. If it doesn't look this way, then the probe isn't tuned.

❖ Go to the probe.

 This is a piece of equipment which goes into the magnet from the bottom. It has cables and hoses attached.



- ❖ With the supplied tool, turn the tuning rod so that the curve aligns with the vertical red line and the matching rod to make the curve reach all the way to the zero line of Y axis. Go back and forth between tuning and matching for optimization.



You can also look at the preamplifier box called HPPR (a small box with cables next to the magnet) and minimize the number of LEDs lit on the horizontal (tune) and the vertical (match) LED arrays, normally 3 green LEDs lit for match and 1 green LED (and maybe a yellow one) lit for tune.



To tune probe from nucleus X (e.g. ^{13}C) to Y (e.g. ^{29}Si), filter on the HPPR box, tuning rod and range rod on the probe need to set correctly according to the tuning table given to the probe. Use a large WBSW (e.g. 60MHz) in WOBB at first and 4MHz at the end for fine tuning.



❖ Tune and Match ^1H channel:

After the ^{13}C channel is optimized, click on , or press the CHANNEL SELECTOR on HPPR, to switch to ^1H and wait until the ^1H curve occurs (takes ~20s). Adjust the Tuning and Matching Rods for ^1H (located on the opposite side to the ^{13}C tuning/matching sticks. The rod labeled with T is for tuning and M for matching) to optimize ^1H .

- ❖ If ^1H tuning have changed significantly, go back to ^{13}C by clicking on , or pressing the CHANNEL SELECTOR on HPPR, and check its tuning. Make adjustment if necessary.
- ❖ Click on  to quit the probe tune/match process.

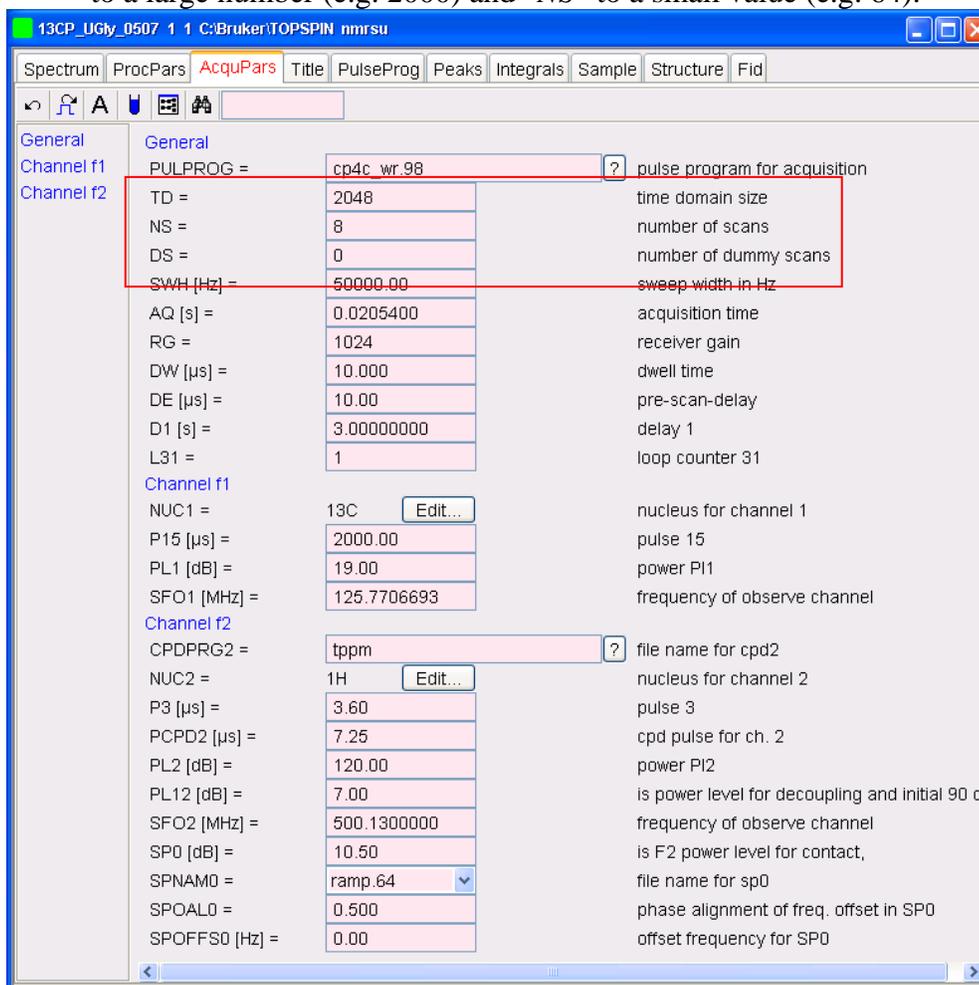
7. Click on **Acquisition Pars**  [ased] for modification of parameters. Make necessary changes of parameters such as “TD”, “NS”, “DI” and maybe “SFOI”. Changes are saved automatically.

 The acquisition time AQ is normally around or less than 20ms. Increase in TD could result in too long an AQ, which could lead to probe or sample damage. Be really care!!!

 Please check pulse lengths and power levels to make sure they are for the probe in use. If not sure, check with Jerry or other proficient users.



For solid-state NMR, it is better to use a loop for “NS”, namely, use a pulse program with `_wr` for parameter “PULPROG” and set loop “L31” to a large number (e.g. 2000) and “NS” to a small value (e.g. 64).



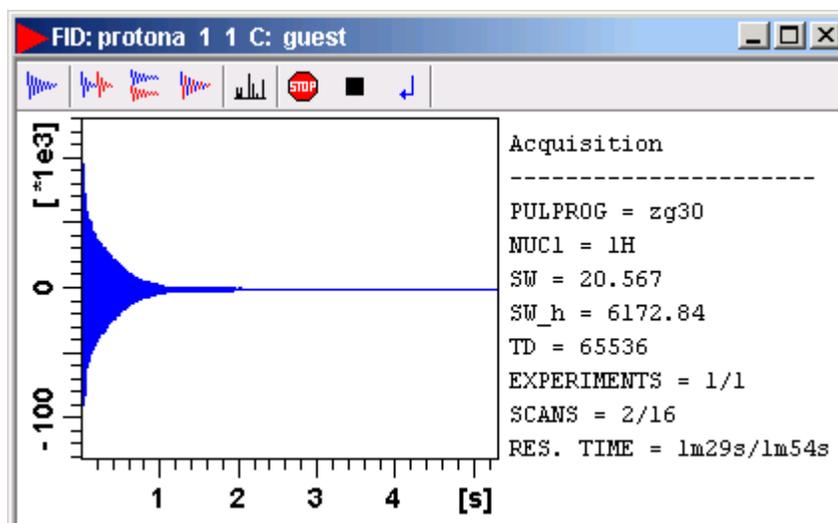
- Click on **Receiver Gain**  and set Options to “Set RG value manually”. Typical values are 16k (512 on 500MHz WB) and 256 (16 on 500MHz WB) for X (^{13}C , ^{29}Si , ...) and ^1H , respectively.



Input a RG value and click **OK**. If the suggested RG value is too high, i.e. the first scan is truncated vertically, reduce rg until the first scan intensity is half of the display window.

- Click on **Start Acquisition**  [zg]. (: If a warning message occurs, make sure to start acquisition in the right dataset). The FID display window below will appear along with some status parameters.

 If parameters are not shown, right-click in the FID window, choose “Display Properties”, check “Status Parameters” and click on **OK**.



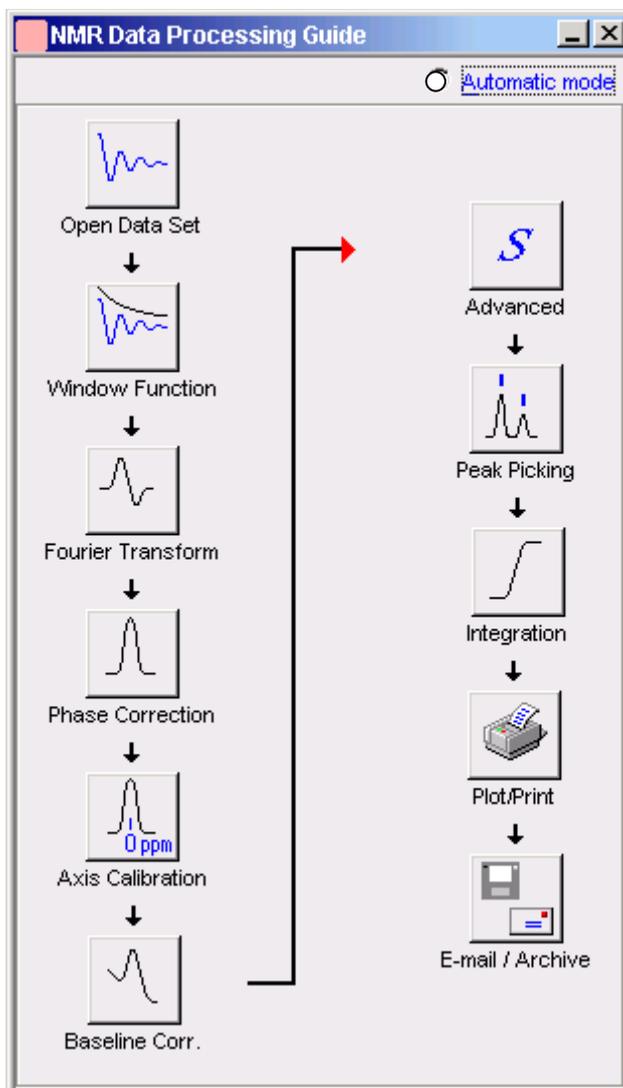
Three of the buttons near the top of the window may be used to:

-  Stop the acquisition [**stop**] with the data in buffer discarded
-  Halt the acquisition [**halt**] with the data in buffer saved to disk
-  Close the FID window

 To monitor the acquisition status, just look at the Status Parameters to the right of FID. When Res. Time = 0, acquisition is completed and it is time to process the raw data.

Click  to close the FID window once acquisition finishes.

- Click on **To Processing**  to start the Data Processing Guide, the counterpart of the Data Acquisition Guide. Follow through the steps in the window popping up.



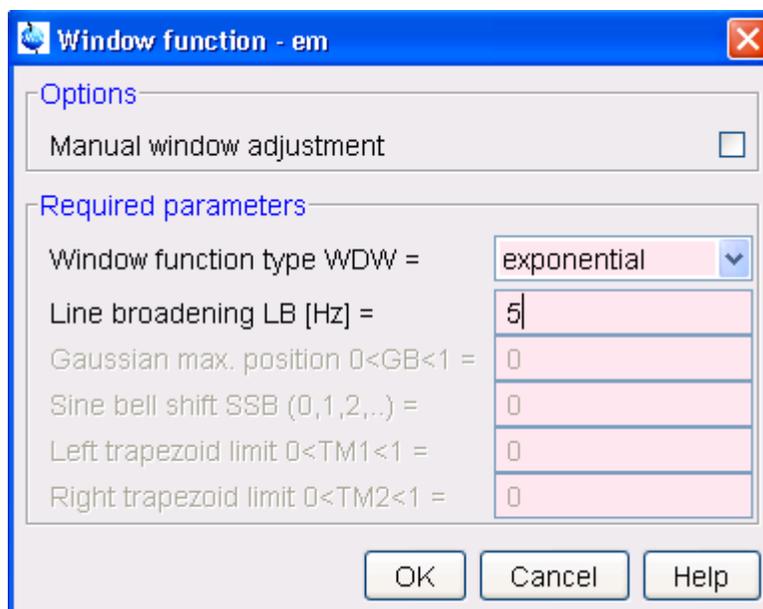
VI. NMR Data Processing

The interactive mode, i.e. with the Automatic Mode unchecked, walks you through the data processing step by step. (See [Appendix A. 1D Data Processing Details](#)).



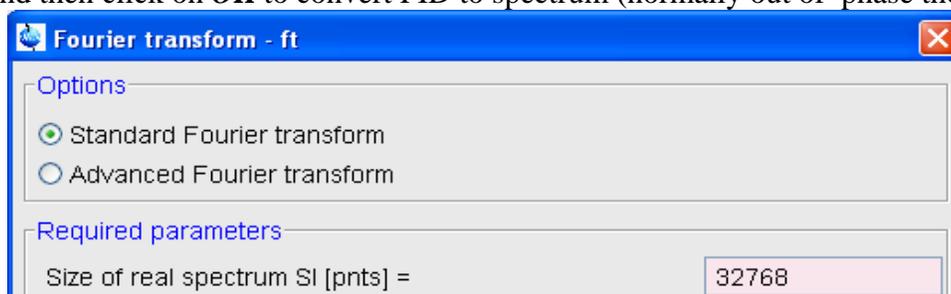
Please note that the first button **Open Data Set**  can be skipped if you process the data just acquired and shown in the active window. Otherwise, use this button to open a different dataset for processing.

- 1) Click on **Window Function**  and set “Line Broadening LB (Hz) =” to appropriate number (normally between 5 and 25Hz) and “Window function type WDW =” exponential, followed by **OK**.



LB is a parameter to reduce noise level at the expense of resolution. The larger the LB, the better the S/N ratio but the worse the resolution. Typically LB = 5 Hz and the exponential WDW ($\text{Exp}(-lb*t)$) is multiplied with the raw data FID to generate a new FID with suppressed noise. [See [Appendix B. LB and Window Function](#) for details]

- 2) Click on **Fourier Transform** , and set
 “Standard Fourier Transform”
 “Size of real spectrum SI = 32768”
 and then click on **OK** to convert FID to spectrum (normally out of phase though).

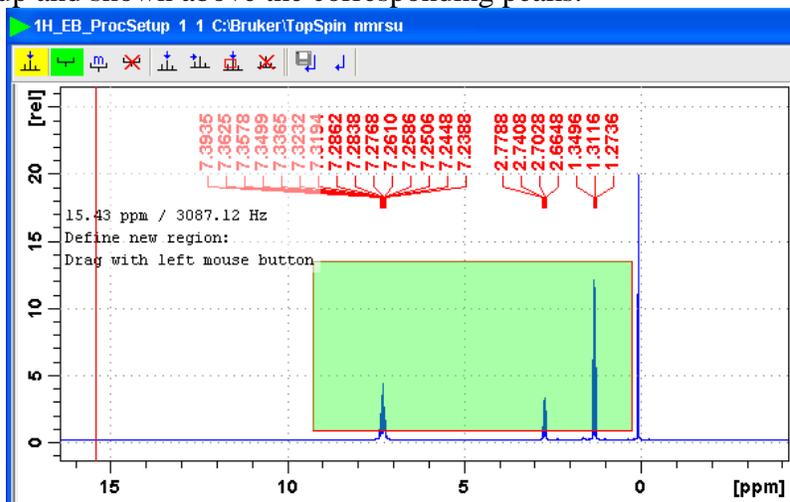


To see the processed spectrum, click on **Spectrum** in the toolbar of data window.



- 3) Click on **Phase Correction**  and check “Automatic Phasing” followed by **OK [apk]**. A phase corrected spectrum is obtained. If not, see [Appendix A. 1D Data Processing Details](#) for manual manipulation of phase correction.

- 4) Calibration: two options here
- if you know the chemical shift value of any peak in the spectrum, expand that peak, click on button **Axis Calibration**  and follow the on-screen instructions.
 - Otherwise, run a standard sample with a known chemical shift, calibrate the spectrum as above, and take the SR value from the ProcPars table to the spectrum to be referenced.
- 5) Click on **Baseline Corr.**  and check “Auto-correct Baseline using Polynomial” [*abs*] followed by **OK** to flatten the baseline of spectrum. If this automatic correction does not work well, you may have to use the option “Correct baseline manually”.
- 6) (**Optional**) **Advanced** : for multi-spectra display, add/subtract, and deconvolution (See [Appendix C. Multi-Display](#) for details).
- 7) Click on **Peak Picking** , choose “Define regions/peaks manually, adjust MI, MAXI”, and click on **OK**. In the data window, drag with the left mouse button a box (green) which defines MI (min. intensity), MAXI (max. intensity), by the bottom and top sides of the box, respectively, and chemical shift limits by the left and right sides. Peaks falling in this box both intensity- and shift-wise will be picked up and shown above the corresponding peaks.

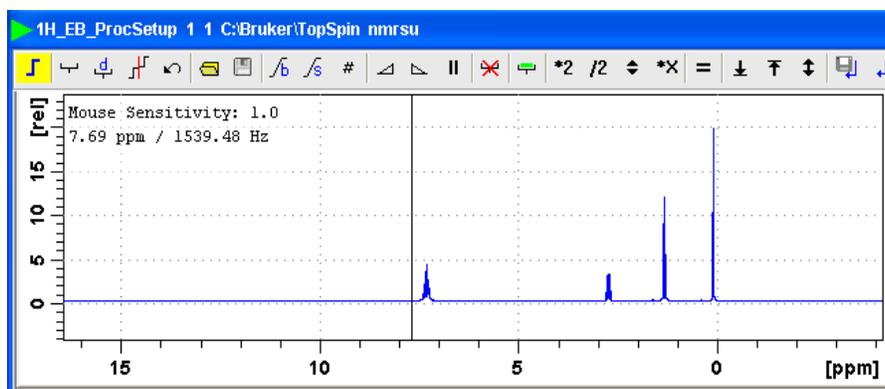


To modify the box, click on  and drag sides or corners.

To delete the box, click on .

To save the peak picking values, click on .

- 8) Click on **Integration**  and choose “Define Integral Regions Manually” followed by **OK**. An integration window appears with the corresponding toolbar displayed at the top of spectrum:



 If you see integration labels and values in the window opened up, delete them first by following the procedure “How to delete integral regions” below.

How to Define Integral Regions and do Integration interactively:

- a. Click the following button (button turns green):
 Define integral region interactively
- b. Put the red cursor line on one side of a peak or multiplet.  For accurate results, make sure the integration starts and ends at the baseline, and D1 is long enough).
- c. Left-click-hold and drag the cursor line to the other side of the peak or multiplet.
- d. Do step 2 and 3 for all regions to be defined and integrated.
- e. Click the  button to save integration and leave the integration mode.

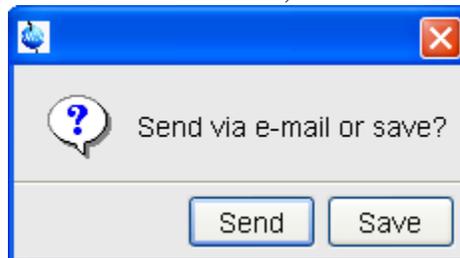
How to delete integral regions:

- To delete all integral regions, click  to Select/Deselect all integral regions, and click  to Delete selected integral regions from the display
- To delete a single region, right-click on the region to be deleted and choose “Select/Deselect” and then click on the delete button .

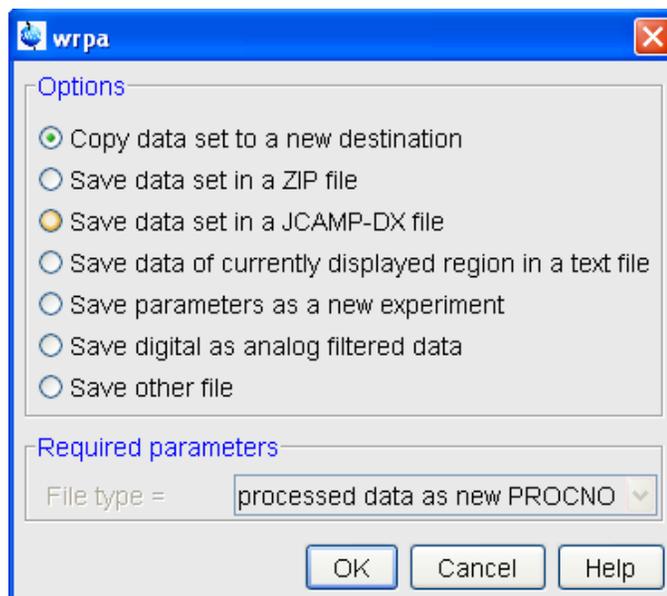
- 9) Click on **Plot/Print**  and check “Print Active Window [*prnt*]”, or check “Print with Layout – start Plot Editor [*plot*]”, followed by **OK**. The former will print what you see in the TopSpin data display window while the latter uses the more sophisticated PlotEditor program for more controlled printing. (See [Appendix D. Plot Editor](#) for details.)

 To Export Data, go to *File* → *Export ...*, specify a folder in the “Look in” box, give a filename in the “File name” box with one of the “Legal File Extensions” shown in the “Files of type” box (e.g. 1H_5pEB.png), and click on the “Export” button.

- 10) (Optional) Click on **E-mail/Archive**  to send the NMR data by email or archive it for storage. Since emailing data is prone to problems, archiving data is a better choice. In the E-mail/Archive window, choose “Save”



Then select one of the choices in the next window (e.g. “Copy data set to a new destination” in this example or “Save data of currently displayed region in a text file”, which is a portable **ASCII** file) followed by **OK**



Change DIR to the destination of your choice (e.g. E:, a flash drive) and click **OK**.

VII. Finishing up



YOU ARE NOT FINISHED WITH THE SPECTROMETER UNTIL YOU DO THE FOLLOWING.

- Click on the **MAS**  button → Click **WB4** → Click **Mode**, in the pop up window, click **Stop**, wait for spinning to go down to zero, and click **Eject**.
- Unpack your sample and clean rotor, cap, packing tools, and bench.
- Close the windows for MAS and other child windows of TopSpin by clicking on the X at the top-right corner of each window.
- Exit TopSpin by clicking the X at the top-right corner of the software.

- e. Logoff your account: click *Start* (bottom-left corner) and choose *Log Off* followed by *Yes*.
- f. **Important:** On the logsheet, record your stop and duration times, and the spectrometer status. Report problems if any.

IX. Appendices

A. 1D Data Processing Details

a. Process data

i. Set line broadening

type [*lb*], then enter a number
typically 5 Hz for ^{13}C

ii. Type [*ef*] ($ef = em + ft$)

This command baseline corrects, exponentially multiplies, and Fourier Transforms the data. You will now be switched over to the spectrum window (frequency domain) and see an unphased NMR spectrum.



[Appendix B. LB and Window Function](#)

b. Phase the spectrum (make all peaks absorptive)

i. Click on button (in the upper toolbar) and the toolbar above your spectrum should look like this:



ii. Move the red cursor line to the tallest peak, right-click there, and select Set Pivot Point to mark the peak with a vertical red line, indicating a pivot point to be used by Ph1. Right-click again and choose “Calculate Ph0”. The tallest peak will now be phased roughly right.

iii. Click and hold on (zero order phase, used when the phase of peaks is frequency-independent). Dragging the mouse will change the zero order phase. Make the tallest peak exactly absorptive.

iv. If other peaks are still not leveled on both sides, Click and hold on

 (first order phase, the phase of peaks is directly proportional to their frequency positions relative to the pivot point set above). Dragging the mouse to fix their phase. Many times this will also straighten out the baseline.

v. Click on to save the phase values and leave the phase mode.

vi. If you want to process the same data again after you have done phasing, use [*efp*] ($efp = em + ft + \text{phase}$) instead of [*ef*], so you don't have to do [*phase*] again.

c. Calibrate the spectrum (if necessary)

1) Locate the solvent or TMS peak of known chemical shift, and expand its nearby region by click - hold - dragging across the peak.

2) Click on  button.

3) Go to the top of the reference peak chosen in 1) and enter the chemical shift value of that peak (the solvent table on desk may help).

d. Integrate peaks



It might be easier to zoom in on a small region before integrating and use the buttons to move around during integration for better differentiation of peaks.

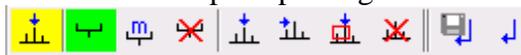
- 1) Type [*abs*] to flat the baseline.
- 2) Click on to enter the integration mode. The toolbar below for integration shows above your spectrum:



- 3) Click on and then on to delete all the integrals originated from step 1).
- 4) Click on for manual integration.
- 5) Drag from one side of a peak to the other to integrate this peak.
- 6) Repeat step 5) for each peak or group of peaks of interest.
- 7) For more accurate integration, click – hold on and move the mouse to flat the left tail of an integral and use for the right tail.
- 8) Once done with all peaks of interest, click on to save the integration values and leave the integration mode.

e. Peak-picking

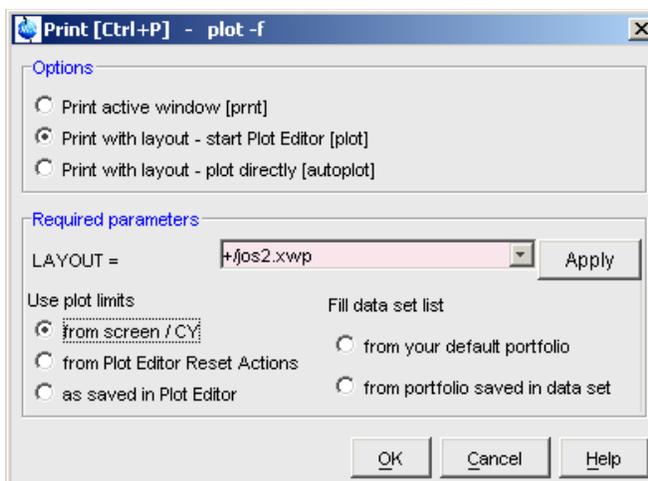
- Click on to start peak picking and show the corresponding toolbar:



- Draw a box to define the peak picking range (vertical sides of the box) and intensity limits (horizontal sides of the box) by placing the cursor at the click – holding the LMB and dragging from the top left corner of the box towards the bottom right corner.
- Peaks falling in that box are automatically picked up and labeled.
- Click on to save the chemical shift values and leave the peak picking mode.
- If necessary, click to delete a peak picking region

f. Plot Spectrum

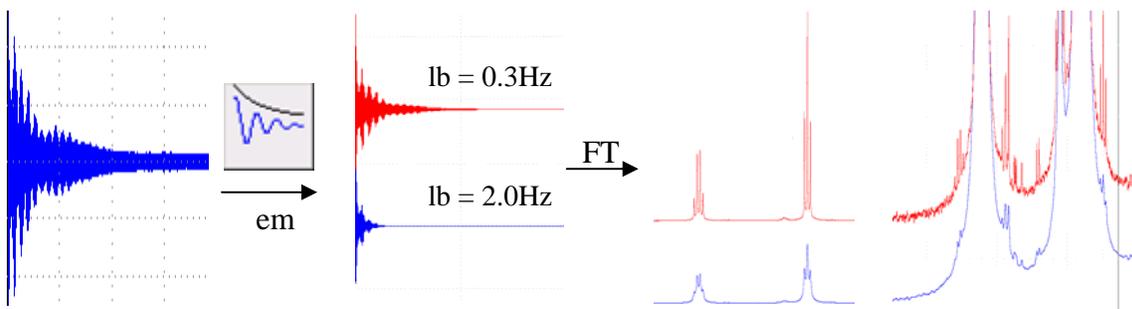
Click on in the upper toolbar, the following window appears:



Turn on the first radio button to print the active window or the 2nd button for the more powerful PlotEditor. (See [Appendix D. Plot Editor](#) for details.)

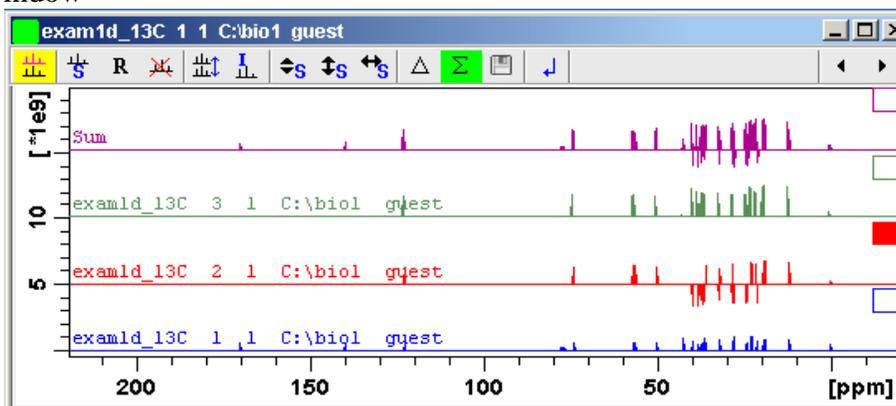
- g. To save spectrum as an electronic file:
- 1) Insert a flash drive or a ZIP disk into computer.
 - 2) In TopSpin or Plot-Editor, go to “File” → “Export” →
 - 3) Specify the destination folder (e.g. where the flash drive or Zip is), filename and file format (e.g. ¹H_NMR.png, .jpg, .tif, ...) → **Export**.
 - 4) Unmount flash drive or ZIP.

B. LB and Window Function



C. Multi-Display

1. Read a 1D dataset by right-clicking on it and choosing “Display” in the browser/portfolio.
2. Click button  in the upper toolbar. The data window will switch to multiple display mode.
3. Add a dataset as follows:
Left-click-hold the dataset in the browser/portfolio and drag it into the data window

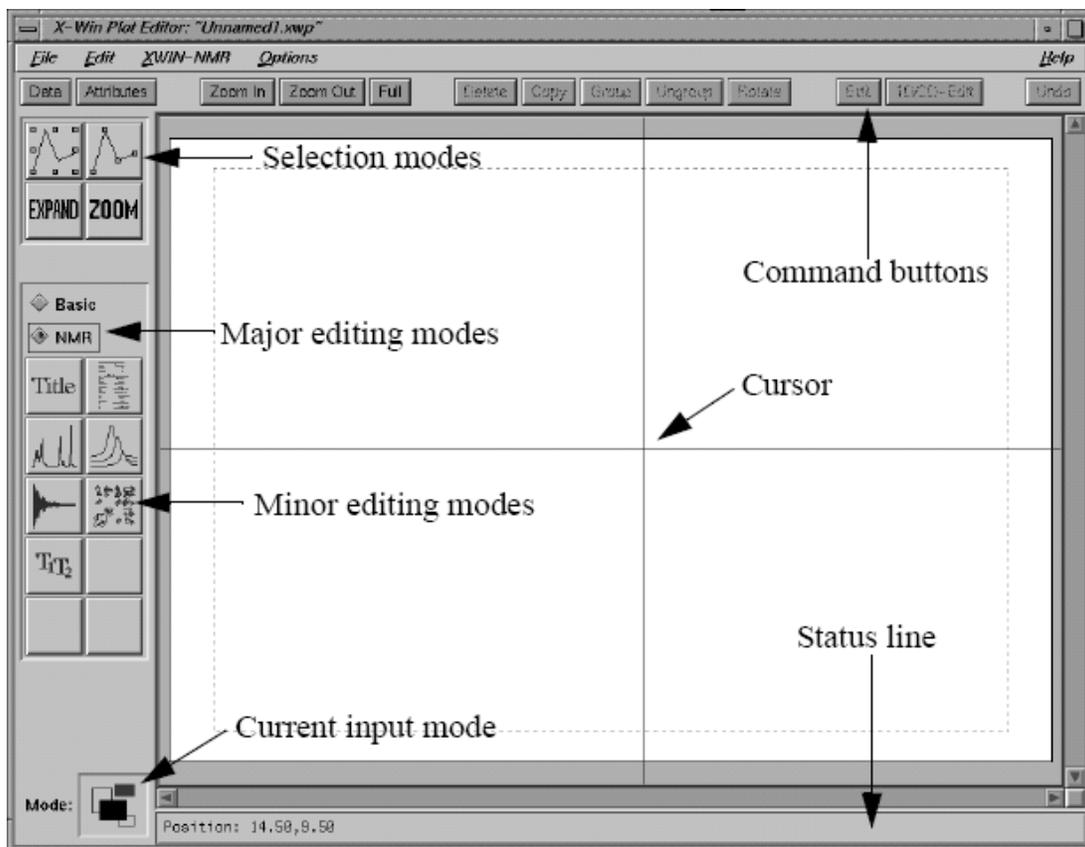


Use the toolbar of the multi-display window for further manipulation and move the mouse cursor over each button for help or refer to the TopSpin Users' Guide for more details.

D. Plot Editor

In the *File* → *Print* window, if you select “Print with layout - start Plot Editor [*plot*]” option and click **OK**, the Plot Editor will be started. This option is equivalent to entering *plot* on the TOPSPIN command line.

This is a very nice and user-friendly program. You are referred to the Plot Editor manual of TopSpin for more details and encouraged to use it often for more controlled printouts.



E. Introduction to Solid-State NMR

a. What is solid-state NMR ?

NMR spectroscopy is performed directly on the samples in solid states or in oriented pseudo-solid phases, for example:

Solid-state samples

Solid-state	Example Materials
Powder	Anything powderable: Amino acids, Organic compounds, Inorganic materials, ...
Single Crystal	Anything forming single crystals: Organic, Inorganic, Biological, ...
Chunk Solid Materials	Machinable to cylindrical shapes to fit into MAS rotors: polymers (plastic, ...)
Film	Stand-alone films or supported on surfaces
LT Liquid and Slurry Materials	Anything which can solidified: solvent, dissolved solute, protein, etc.

Oriented pseudo-solid phases: Liquid crystal, Lipid, etc.

b. Why Solid-state NMR ?

It is desirable to run NMR experiments in solid-states when

- Samples are not dissolvable.
- Properties change after dissolution.
- Intermolecular interaction or local asymmetry is important: CSA, Dipolar coupling, quadrupolar interaction, J-coupling, etc.

c. Differences between conventional solution NMR and Solid-state NMR:

In solution: J-coupling, in the order of a couple of hundred Hz at most, dominates under fast tumbling of molecules, and high resolution spectra prevail in most cases.

In Solid-state: Other than J-coupling, there are other overwhelmingly dominating interactions intra- or inter-molecularly:

Interaction	Strength
J	Hz
CSA	Up to ~2000 ppm
Dipolar	Up to tens of kHz
Quadrupolar	Up to tens of MHz

These are the factors which broaden the NMR lines in solid-state. To get high resolution solid-state NMR spectroscopy, the following methods have been used to average out the interactions above in solids:

- Spatial averaging: Sample Spinning (MAS, DOR, DAS)

- Spin averaging: Multiple RF Pulses (MQMAS, Dipolar Decoupling---CRAMPS)

Thus, solid-state NMR experiments are normally performed at **high sample spinning and high RF power**.

On the other hand, these interactions provide us with a lot of structural information, such as distance, dihedral angle, H-bonding, etc., and are important to our research. Therefore, a compromise may be made between high resolution and the retention of the interactions to the extent where structural information can still be retrievable.

F. Online NMR Book and Bruker NMR Encyclopedia

- 1) NMR Book: <http://www.cis.rit.edu/htbooks/nmr/>
Introduction to NMR concepts and practical issues.
- 2) NMR Guide & Encyclopedia: <http://www.bruker.de/guide/>
All you want to know about NMR.

G. Requirements for Access to the MRL NMR at CNSI

You have to pass the mini quiz within one month after training in order to be qualified for access to the NMR facility of MRL, which includes:

- Key Card for Lab & Building Authorization Form (see Sylvia in Rm. 2066G for)
- Web Scheduling Account (email Jerry for a setup appointment)
- NMR Account (email Jerry for a setup appointment)

These requirements apply to both on- and off-campus users.